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MUTLIDIMENSIONAL NANOSCOPIC APPROACHES TO NEW THERMOELECTRIC MATERIALS (POSTPRINT)

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Multidimensional nanoscopic approaches to new thermoelectric materials

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ABSTRACT

The advantages of thermoelectric energy conversion technologies are briefly summarized. Recent material advances are discussed, with the focus on one-dimensional (1-D) self-assembled molecular materials as building blocks for new thermoelectric materials. The preparation, doping, and thermal characterization of phthalocyanine based materials are presented. The thermal conductivity of the doped material is lower than the undoped material even though the electrical conductivity of the doped material is orders of magnitude higher than the undoped material. This is counter intuitive against the backdrop of the Wiedemann-Franz treatment of thermal conductivity in electrical conductors from which one would expect thermal and electrical conductivity to both increase with introduction of additional charge carriers. These unusual results can be understood as a competition between the generation of an increased number of charge carriers and enhanced phonon scattering resulting from the introduction of chemical dopants. The thermal conductivity of the undoped phthalocyanines has been found to be small and only modestly temperature dependent in the 50-300 C range, but it is larger than a previous, indirect measurement.

Keywords: thermoelectric, thermal conductivity, phthalocyanine, thermal conductivity, one dimensional, energy harvesting

1. INTRODUCTION

In comparison with more well-known energy harvesting technologies, thermoelectric devices offer distinctive advantages. The closest analog to a thermoelectric energy harvesting or power generating device is the photovoltaic as both are solid state devices that rely on excitation of charge carriers within semiconductors and produce DC currents. However, photovoltaic arrays are limited to daylight hours, whereas thermoelectric modules operate as long as a suitable thermal gradient is present. Batteries of course store energy, while fuel cells convert fuels to electric energy: neither harvest energy in their own right.

Thermoelectric energy inter-conversion technologies can be applied rather diversely: (1) for energy harvesting of waste heat by converting heat directly into electric current via the Seebeck effect; (2) for primary power generation from almost any heat source; (3) for cooling and refrigeration via the Peltier effect; (4) for precise temperature control of electronic and optical components; (5) for heat pumping and thermal lift to convert low grade waste heat into a higher quality heat for better heat rejection. More than one of these applications can be combined in one device. For example, the use of thermoelectric elements on satellites to control the direction and flow of heat by sandwiching the thermoelectric elements between individual components and a thermal bus has recently been proposed¹. Such a configuration allows efficient thermal management of each component by its own thermoelectric element.

The global economic potential of efficient and cost effective thermoelectric units for energy harvesting is tremendous: it has been estimated that about 90% of primary power generation relies on heat engines², with the majority of the energy lost as waste heat. As shown in Figure 1, two thirds of residential energy consumption is related to heating or cooling,

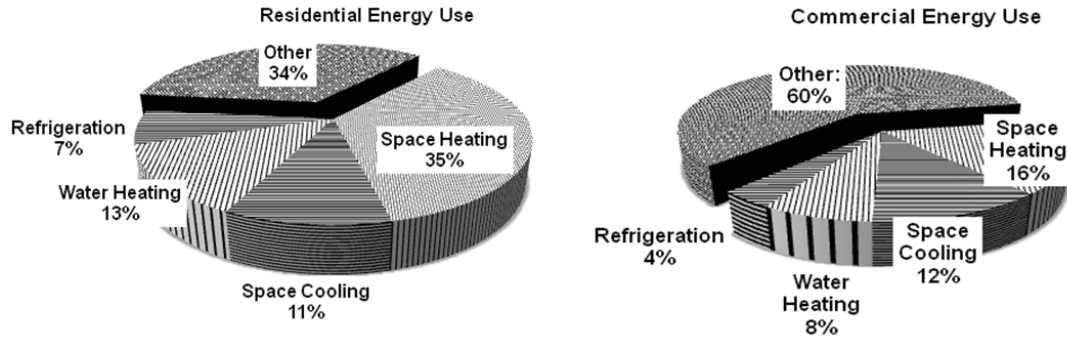


Figure 1: Residential and commercial thermal energy utilization (data from reference 3)

while 40% of commercial energy utilization is related heating or cooling. While not energy harvesting *per se*, in the broader energy picture the impact of cost effective, efficient thermoelectric heating, cooling and electricity production make them compelling targets for researching new materials and device configurations.⁴

Perhaps the best features of thermoelectric devices is summed up by the following characteristics: long life (> 30 years), maintenance free operation, no moving parts or vibrations, reversibility, independent of g-forces or orientation, no electromagnetic emissions, precise control. While it is commonly held that thermoelectric refrigeration is much less efficient than compression based methods, this is in reality only true at larger scales. As the size of a system diminishes, thermoelectric cooling or energy harvesting can become preferred from a systems perspective. For example, the specific energy of a high efficiency Stirling engine at 25 kW is 220 W/kg, a 5 kW NASA Stirling system is 5 W/kg, whereas a bismuth-telluride based thermoelectric at 14.7 W has a specific energy of 300 W/kg. The impacts of thermoelectric device designs⁴, materials⁵, and their limitations⁶ are discussed in greater detail in the literature.

2. NEW MATERIALS

Thermoelectric devices and materials are typically compared based on the dimensionless figure-of-merit, ZT where Z is defined in equation 1, σ is the electrical conductivity (S/m^{-1}), S (or often α) is the Seebeck coefficient (V/K), κ is the thermal conductivity (W/mK), and T is the absolute temperature (K). For decades the two workhorse materials for thermoelectric

$$Z = \frac{\sigma S^2}{\kappa} = \frac{\sigma S^2}{\kappa (\text{electron} + \text{phonon})} \quad (1)$$

Thermoelectric devices have been variants of Bi_2Te_3 and $SiGe$, the former for modest temperatures latter for higher temperature applications, both with $ZT \sim 1$. A resurgence of interest in new thermoelectric materials occurred when Hicks and Dresselhaus⁶ predicted significant increases in ZT , up to ~ 14 , for 1-D materials. This predicted enhancement in ZT arose from two effects: inhibition of thermal transport due to phonon scattering from the surfaces of the wires, and confinement of the electrons in 1-D. While the predicted $ZT \sim 14$ materials have remained elusive, this work stimulated the field and did result in significant advances among several fronts. Many of the recent advances in thermoelectric materials since the Hicks and Dresselhaus paper have been summarized recently in several review articles.⁷⁻⁹

Casian¹⁰⁻¹⁴ et al. published a series of papers detailing theoretical analysis of what can be called 1-D, self-assembled molecular nanowires but have also been known by other terms including molecular metals (or semiconductors), charge transfer salts, organic metals or organic semiconductors, or π -stacked conductors among others. Such materials are composed of 1-D stacks of planar building blocks loosely held together by van der Waals and π - π interactions. Electrical conductivity is typically introduced by chemical doping that adds (chemical reduction, n-doping) or removes (chemical oxidation, or p-doping) electrons from a fraction of the molecules in the stack. Using what appear to be reasonable values for transport properties, treatment of such materials using the Boltzman kinetic model suggested a ZT as high as ~35 could be obtained.

From a chemical physics picture, it makes sense that such materials might have large ZT. The thermal conductivity along the stacking direction should be very small as the intermolecular interactions are non-bonded. This intermolecular interaction along the stacking direction is akin to the interplanar interactions in graphite, in which the thermal conductivity is known to be small. By contrast, the electrical conductivity along the stacking direction can be quite high, which historically lead to the phrase “molecular metal.” Thirdly, construction of the stacks from molecular building blocks can give enhanced Seebeck coefficients as seen from the dependence of the Seebeck coefficient on the density of states.

Equation 2 shows the dependence of the Seebeck coefficient for a semiconductive material on the density of charge carriers and the mobility of the carriers, where k_B is the Boltzmann constant, q is the charge on the carrier, $\sigma(E)$ is the energy dependent electrical conductivity, n is the number of charge carriers, μ is the charge mobility, and T is absolute

$$S = \frac{\pi^2 k_B}{3 q} k_B T \left\{ \frac{d[\ln(\sigma(E))]}{dE} \right\}_{E=E_F} = \frac{\pi^2 k_B}{3 q} k_B T \left\{ \frac{1}{n} \frac{dn(E)}{dE} + \frac{1}{\mu} \frac{d\mu(E)}{dE} \right\}_{E=E_F} \quad (2)$$

temperature. Semiconductors constructed from molecular building blocks have a proclivity form narrow bands as illustrated in Figure 2. The electronic bands along the stacking direction of phthalocyanines are thus generally narrow,

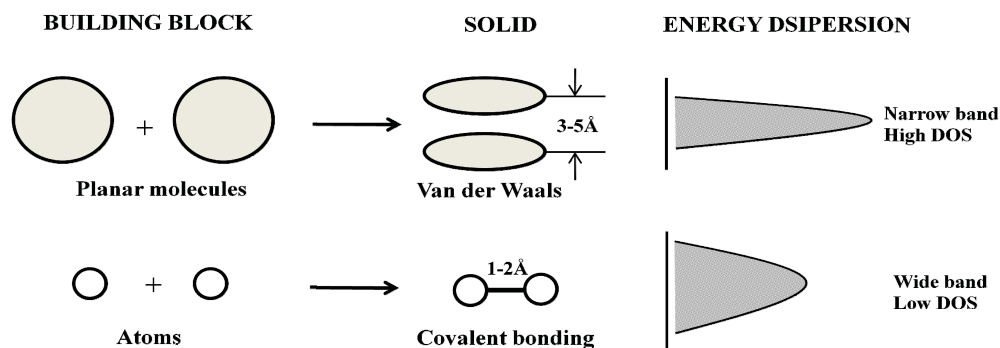


Figure 2: Electronic Density of State (DOS) characteristics resulting from molecular and covalent interactions

which is a natural consequence of their construction from non-bonded molecular units. This should lead to larger thermopowers, and this has indeed been found in selected examples such as certain phthalocyanines as discussed below. In terms of chemical design, such structures have all three parameters defined in equation 1 in the right direction. While combining all these properties in one material to produce the values predicted by Casian is unlikely, achieving only 10-20% of the values predicted by Casian (ZT ~2-3) would nonetheless be a monumental breakthrough with far ranging societal impact.

3. PHTHALOCYANINES

3.1 General Characteristics

There are perhaps thousands of candidate 1-D charge transfer materials that could fall within the framework espoused by Casian. Many are laboratory curiosities that have only been prepared on the gram scale or smaller. Many are not thermally stable, and often tedious methods are required for their preparation.

Phthalocyanines fit within the Casian framework, but offer distinct advantage including high thermal stabilities, outstanding electrical conductivities when doped, and excellent photochemical stabilities. They are used as pigments and dyes, catalysts, and photodynamic anticancer therapeutics. A metal is usually in the center of the phthalocyanine ring structure, as shown for nickel phthalocyanine in Figure 4. The challenge is to tailor phthalocyanines for desirable

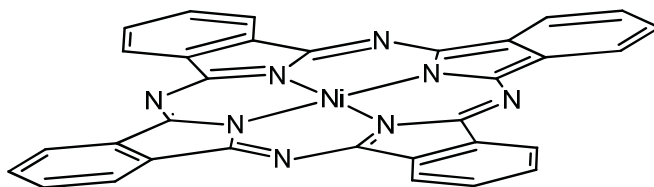


Figure 3: Chemical Structure of Nickel Phthalocyanine

thermoelectric characteristics. Varying the metal in the middle of the phthalocyanine framework should allow for tailoring of the electronic properties with minimal impact on thermal conductivity.

When oxidatively doped, most phthalocyanines become p-type semiconductors due to partial oxidation of the Pc ring. Electrical conduction then occurs as the resulting hole travels from one phthalocyanine ring to another. Besides

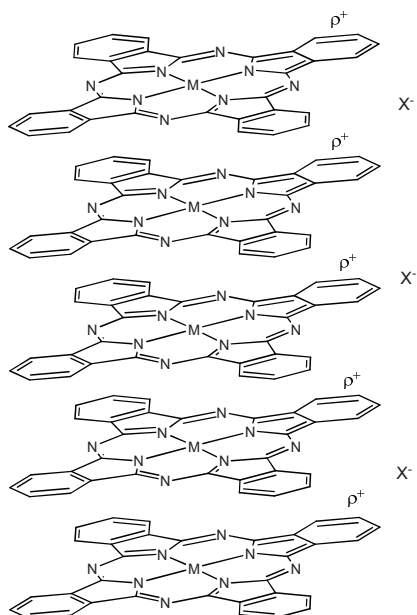


Figure 4: Schematic Stacking of Oxidatively Doped M-Phthalocyanine (X^- = dopant counterion)

introducing charge carriers, the dopant counterions sit rather loosely in the lattice which should serve to lower the thermal conductivity via vibrational effects.

Nanoscale metallic and semiconductor wires formed from atomic constituents have low thermal conductivities. As the diameter of the wire becomes less than the phonon mean free path, phonon scattering off the wire surface restricts thermal transport along the wire.^{2,15,16} In 1-D wires built from molecular components a similar effect should hold, but the thermal conductivity will be further lowered since the intermolecular interactions between the building blocks are noncovalent. The interactions along the wire direction is non-continuous, that is, not based on chemical bond linkages but is more akin to the weak interactions between graphite planes.

The aim of this work was to prepare pure phthalocyanine materials, characterize the thermal conductivity of the undoped materials, then oxidatively dope representative phthalocyanines by high temperature processes and examine the effect of the dopant on the thermal conductivity.

3.2 Synthesis

Preliminary investigation showed that nominally pure commercially available materials were in fact contaminated with 7-8% chlorine which proved difficult to remove. Subsequently, all metal phthalocyanine materials were synthesized and purified in-house. The following is typical of the procedure followed, based on published approaches.¹⁷

Synthesis of Nickel Phthalocyanine: Into 1L 3-neck RBF equipped with a mechanical stirrer was added phthalonitrile (18.34 g, 0.14 mol), nickel (II) acetate tetrahydrate (8.71 g, 0.035 mol) and dimethylformamide (150 mLs). The mixture was heated to reflux (160 °C) while being stirred under an inert atmosphere for 48 hours. The resulting mixture was filtered to yield a purple solid which was then Soxhlet extracted with water for 24 hours and dried under vacuum at 100 °C for 12 hours. The crude product was sublimed <0.01 torr at 450 °C for 8 hours, resulting in 11.6 g of purple crystals (58% yield). Anal.: Calc. for $C_{32}H_{16}N_8Ni$: C 67.28, H 2.82, N 19.62, Ni 10.28%. Found: C 67.13, H 3.01, N 19.52, Ni 9.98%.

Synthesis of Iodine doped Nickel Phthalocyanine: Into a 50mL glass ampoule was added nickel phthalocyanine (2.00 g, 0.0035 mol) and iodine (I_2 , 1.35 g, 0.0053 mol). The glass ampoule was cooled in a water bath (~ 5 °C) to ensure limited evaporation of the iodine and then sealed under 0.01 torr. The glass ampoule was placed into a muffle furnace and heated to 520 °C for 6 hours. Once the ampoule was cooled to room temperature, the ampoule was opened and the black crystalline product was rinsed with ethanol to remove excess iodine. The remaining product was dried under vacuum at 60 °C for 12 hours resulting in 2.67 g of black crystals (92.4% yield). Anal.: Calc. for $C_{32}H_{16}N_8I_{.75}Ni$: C 57.7, H 2.4, N 16.8, I 14.3, Ni 8.8%. Found: C 58.0, H 2.4, N 16.9, I 14.8, Ni 8.5%.

3.3 Characterization

All samples were prepared using the following method: sublimed materials were ballmilled to reduce them to a fine powder. The powders were then pressed into 28.8 mm diameter pellets under a compressive load of 20,000 lbs. Thin sheets of plastic were placed between the metal die-head of the press to prevent sample adhesion and reaction with the die itself.

Thermal conductivity measurements were conducted using an Anter Unitherm 2022 Guarded Heat Flow Meter Thermal Conductivity Measuring System which conforms to the ASTM E1530 standard. Since sample diameters were less than the hot plate diameters a correction factor was added per manufacturer instructions. All thermal conductivity measurements were conducted between 50 and 300 °C in fifty degree increments. The thermal conductivity measurements for the undoped phthalocyanines were conducted three times for each sample and values shown in Figure 5 are an average. The doped sample was only tested once due to sample reaction with the hot plate sandwiching metal at higher temperatures. We believe the measurements were not compromised but this degradation, but a confirmation awaits fabrication of a non-reactive coating for the hot plate which is in progress. A calibration was performed as prescribed by the manufacturer using three calibration standards and the error in the measurements as stated by the device manufacturer should be +/- 3% to +/- 8 %.

Electrical conductivities were measured by a two point probe method on ~ 1 mm specimens at room temperature using a Keithly 2425 source meter. The iodine doped phthalocyanines had values in the 10^{-4} S/cm range, whereas undoped phthalocyanines are typically in the 10^{-7} S/cm range.¹⁸

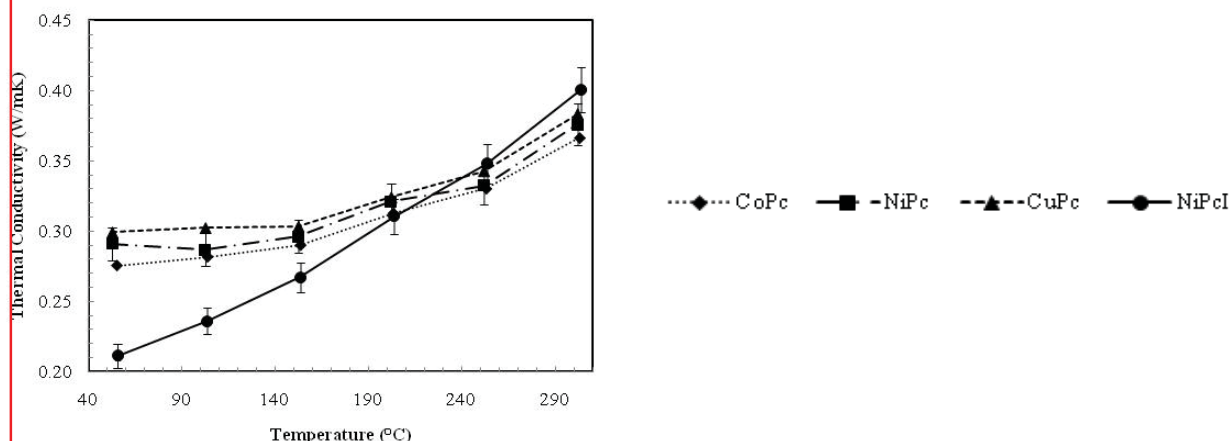


Figure 5: Thermal conductivities of M-phthalocyanines

4. CONCLUSIONS

High purity phthalocyanine compounds have been prepared and processed in pellets. Their thermal conductivity has been found to be low, ~ 0.3 W/mK, which is about an order of magnitude lower than typical thermoelectric materials and in the range expected for molecular based materials. Our thermal conductivity measured on macroscopic pellets by the guarded hot plate method is substantially larger than the value of 0.00158 W/mK estimated¹⁹ from a fit current and grid temperature data from transmission electron microscopic measurements. The ~ 0.3 W/mK is more in line with typical values for molecular and polymeric materials. The thermal conductivity shows only minor variation with the identity of the specific metal in the phthalocyanine ring, and shows only minor variation with temperature in the 50-300 C range. High temperature doping with iodine has been accomplished to yield materials that are stable with respect to loss of dopant at atmospheric conditions. Preliminary thermal conductivity on iodine-doped Nickel phthalocyanine indicates that the thermal conductivity is lower than the undoped material in the 50-200 C range but rises above that of the undoped material about 250 C. The reduced thermal conductivity in the lower temperature ranges can be understood as resulting from increased phonon scattering due to the dopant counterions. However, the thermally activated electrical conductivity well known in doped phthalocyanines results in a significant increase in number of charge carriers as the temperature is increased, and so at the higher temperature ranges, the thermal conductivity of the doped material is above that of the undoped material.

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